

WHAT IS CLAIMED IS:

1. An electrolytic phosphate chemical treatment method of forming a film composed of a phosphate compound and a metal that is reduced and precipitated from an ionic state on the surface of a metal material article to be treated by performing electrolytic treatment on said article to be treated in a phosphate chemical treatment bath by contacting said metal material having electrical conductivity with said phosphate chemical treatment bath containing phosphate ions and phosphoric acid, nitrate ions, metal ions that form a complex with phosphate ions in said phosphate chemical treatment bath, and metal ions for which the dissolution-precipitation equilibrium potential at which ions dissolved in said phosphate chemical treatment bath are reduced and precipitate as metal is equal to or greater than -830 mV, which is the cathodic reaction decomposition potential of the solvent in the form of water when indicated as the hydrogen standard electrode potential, and is substantially free of metal ions other than those which are a component of the film; wherein,

the ORP (oxidation-reduction potential) of said phosphate chemical treatment bath (indicated as the potential relative to a standard hydrogen electrode) is maintained at equal to or greater than 700 mV.

2. An electrolytic phosphate chemical treatment method according to claim 1, wherein said electrolytic treatment preferably uses for the electrode material that dissolves in the treatment bath a metal that forms a complex with phosphoric acid and phosphate ions in the phosphate chemical treatment bath and/or a metal material for which the dissolution-precipitation equilibrium potential at which ions dissolved in the phosphate chemical treatment bath are reduced and precipitate as metal is greater than or equal to -830 mV, which is the cathodic reaction decomposition potential of the solvent in the form of water when indicated as the hydrogen

standard electrode potential, and a metal material that is insoluble during electrolysis.

3. The electrolytic phosphate chemical treatment method according to either claim 1, wherein the amount of Fe ions dissolved into the treatment bath from an Fe electrode, when performing cathodic treatment of said article to be treated and using an Fe electrode as the electrode that dissolves in the treatment bath, is controlled in order to make said ORP of the phosphate chemical treatment bath equal to or greater than 700 mV.

4. The electrolytic phosphate chemical treatment method according to claim 1, wherein in the case the article to be treated is a steel material, the amount of Fe ions dissolved into the treatment bath in anodic treatment in which said steel material in the form of the article to be treated is dissolved as the anode, and the amount of Fe ions that dissolve in the treatment bath from an Fe electrode in cathodic treatment, are controlled so that the ORP of the phosphate chemical treatment bath is equal to or greater than 700 mV.

5. The electrolytic phosphate chemical treatment method according to claim 1, wherein the electrode used in electrolysis for making the ORP of the phosphate chemical treatment bath equal to or greater than 700 mV is an insoluble metal material.

6. The electrolytic phosphate chemical treatment method according to claim 1, wherein a chemical that contains Fe ions which replenishes the phosphate chemical treatment bath is an Fe-phosphate complex in order to make the ORP of said phosphate chemical treatment bath equal to or greater than 700 mV.

7. The electrolytic phosphate chemical treatment method according to claim 1, wherein the ORP of the phosphate chemical treatment bath is equal to or greater than 770 mV.

8. The electrolytic phosphate chemical treatment method according to claim 1, wherein metal ions that form

a complex with phosphoric acid and phosphate ions in the phosphate chemical treatment bath are preferably at least one type of Zn, Fe, Mn or Ca ions.

5 9. The electrolytic phosphate chemical treatment method according to claim 1, wherein NO, NO₂ and/or N₂O₄ gases generated and dissolved in an electrolytic treatment tank are removed from the treatment bath by separating the treatment tank into an electrolytic treatment tank that carries out electrolytic treatment and an auxiliary tank that does not carry out
10 electrolytic treatment, circulating the treatment bath between the two tanks, and providing a mechanism that opens treatment liquid to the atmosphere either between the above two tanks or within the two tanks, as a means
15 of separating NO₂, N₂O₄ and/or NO gas formed in the treatment bath accompanying electrolytic treatment from the treatment bath.

20 10. The electrolytic phosphate chemical treatment method according to claim 9, wherein the auxiliary tank that does not carry out electrolytic treatment has a mechanism in which the treatment liquid is passed through a permeable solid structure.

25 11. The electrolytic phosphate chemical treatment method according to claim 10, wherein the solid structure is a film.

30 12. The electrolytic phosphate chemical treatment method according to claim 9, wherein a filter having a mechanism that filters the treatment liquid is used for the auxiliary tank that does not carry out electrolytic treatment.

35 13. The electrolytic phosphate chemical treatment method according to claim 9, having a liquid circulation circuit that removes a portion of the treatment liquid at a location prior to being introduced into a filter material in a filter, exposes the removed treatment liquid to the atmosphere, and returns it to the electrolytic treatment tank after removing gases in the

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form of nitrogen oxides present in the treatment liquid.

14. The electrolytic phosphate chemical treatment method according to claim 9, wherein the ORP of the treatment bath is equal to or greater than 840 mV.

5 15. The electrolytic phosphate chemical treatment method according to claim 9, wherein the treatment bath is maintained in a constant state by measuring the above ORP value of the treatment bath and changing the amount and/or composition of replenishing chemical corresponding
10 to the change in that value.

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